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Soybean Protein Fibres (SPF)

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1. Introduction

Soybean protein fibres (SPF) are manufactured fibres, produced from regenerated soya *Glycine Max* soybean proteins in combination with synthetic polymer (polyvinyl alcohol) as a predominant component. According to textile fibre labelling (FTC, 2010), textiles from SPF can be marked as azlons from soybean. Azlons are manufactured fibres in which the fibre-forming substance is composed of regenerated naturally occurring proteins (FTC, 2011).

The first commercially successful method for producing regenerated protein fibres was developed by the Italian chemist Antonio Ferretti in 1935 (Ferretti, 1944; White, 2008). In 1936 Snia Viscosa (Milan) started with the production of the world's first commercially produced protein fibres Lanital™ which were made from milk casein (Anon., 1937). Courtaulds in Great Britain (casein fibres Caslen, Fibrolan), Enka in Netherlands, Germany and United States of America (casein fibres Aralac, R-53) soon followed with their commercial productions. Fibres were treated with formaldehyde or aluminium salts, to create cross-links between proteins in the fibre and improve fibre's wet properties. In the year 1945 Snia Viscosa replaced Lanital™ fibres with Merinova™ casein fibres (Fig. 1), which had better properties than Lanital™ fibres.

In the middle of the 20th century and until 1960, vegetable regenerated protein fibres from oilseed peanuts proteins (Ardil fibres, produced by British ICI Company) (Fig. 1) and from corn zein proteins (Vicara fibres produced by American Virginia-Carolina Corporation) were also produced among casein fibres. Fabrics made from regenerated protein fibres were soft, lustrous, resilient, with a good hand and thermal resistance. They were used as a wool or silk substitute by many European fashion designers.

Rapid development of cheaper synthetic fibres with excellent mechanical properties in the early sixties had influence on the commercial production of regenerated protein fibres that was completely discontinued in the middle of the 1960s.

Nowadays, increasing world population need additional quantities of textiles. The world fibre production increases from year to year and in 2010 there was globally produced 78 million tons of fibres, including about one million tons of wool and 0.15 million tons of silk (Kanitkar, 2010). Wool and silk are still very expensive fibres, with selling prices of about 14–23 €/kg and 28–40 €/kg, respectively (Reddy & Yang, 2007).

Today's fibre production strategy is redirected from crude oil to renewable raw materials, eco-friendly and sustainable fibres, that could be biodegraded or recycled. Important raw materials for future textile fibres production could be cheap and worldwide available agricultural by-products, like lignocellulose (from rice straw), wheat gluten (Yang et al., 2006), casein protein from milk after butterfat is removed, zein protein from corn after starch manufacture, and soybean protein after beans are pressed and oil is removed.

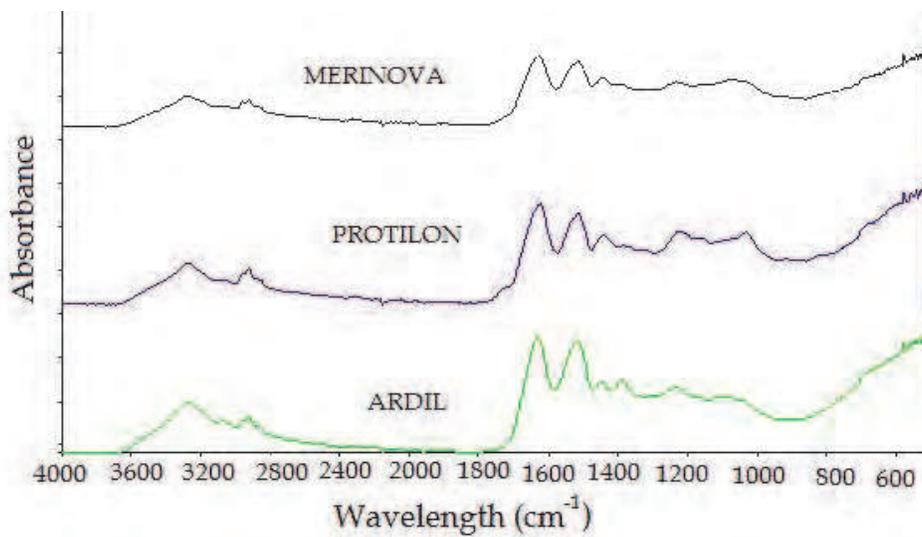
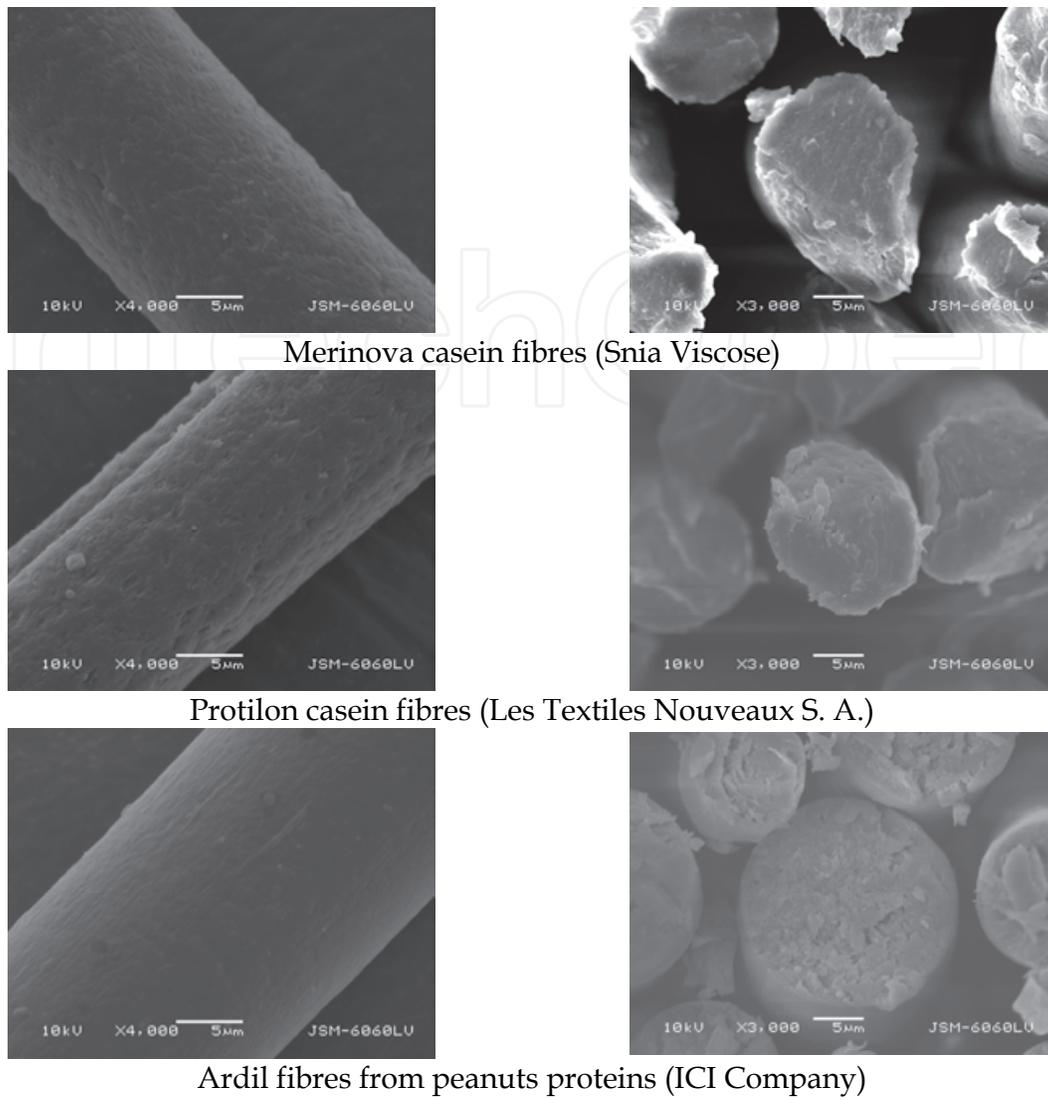


Fig. 1. Scanning electron microscope views and comparative FT-IR/ATR spectra of pure protein fibres with typical absorption peaks at 1658 cm^{-1} (amide I) and 1538 cm^{-1} (amide II).

First protein fibres had low tensile properties, especially in wet state. In order to improve mechanical properties of protein fibres, proteins were combined with synthetic polymers such as acrylonitrile or vinyl alcohol by graft copolymerization or polyblending. First such fibres, made on the patent basis of Morimoto (Morimoto et al., 1962), were produced by the Japanese Toyobo in 1969. The copolymer fibres Chinon® were made from 30% casein and 70% acrylonitrile. Acrylonitrile was grafted on protein with the addition of minor amounts of vinyl or vinylidene chloride for flame retardation. Fibre's density was 1.22 g/cm³, tensile stress in dry state 3.5-4.5 cN/dtex and moisture regain 4.5-5.5%.

Combining natural proteins and synthetic polymers to get fibres with good moisture absorbency and high tenacity led to new researches in the field of fibres at the beginning of the 21st century.

New fibres from casein proteins have been commercialized as milk protein fibres in China by Shanghai Zhengjia Milkfiber Sci& Tech Co., Ltd., under the brand name Zhengjia®. In the year 2005 a Chinese patent for producing the fibres was granted (Shanghai Z., 2011). Milk fibres are chemical casein acrylic fibres made from graft copolymer of casein and acrylonitrile. Fibres contain about 25-30% of milk proteins and 70-75% of acrylic component. The process is ecological (in 2004 it passed the Oeko-Tex Standard 100 green certification) with no formaldehyde content. Milk fibres with about 55% crystallinity have round cross section with many irregular vertical trenches and pockmarks on the surface (Wang et al., 2009). The fibres with linear density 2.22 dtex have breaking tenacity 2.5 cN/dtex and higher, breaking elongation 35.5%, elastic recovery 76.5%, moisture regain 4-5% and bacteria resistance ≥80% (Shanghai Z., 2011). Milk fibres could be dyed with reactive and acid dyes and after treated with crease-resist finishing and softening agents (Arslan, A., 2007, 2008, 2009).

New viscose filament yarn Lunacel, produced by Kurabo Industries Ltd. (Osaka, Japan), has combined properties of vegetable and animal fibres. The fibres are made from cellulose cotton linter pulp that is cross-linked with water-soluble food protein (Kurabo, 2007).

Using animal proteins as raw material for spinning fibres is very expensive. New soybean protein fibres (SPF) from soybean proteins and polyvinyl alcohol were developed in China by G. Li at Huakang R&D Center (Li, 2003, 2007). The fibres are first manufactured fibres, invented by China. The production process for new fibres was laboratory established in 1993 and commercially promoted in 2000. In 2001 the fibres were standardised and in 2003 they were launched.

The objective of this study was to investigate the contemporary SPF biodegradation in soil at controlled laboratory conditions.

2. Soybean protein fibres

2.1 Fibre forming soybean proteins

Soybeans are very rich with proteins (about 37-42% of dry bean) (Krishnan et al., 2007) in comparison to milk (3.2%), corn (10%) and peanuts (25%). Soybean proteins are used for food and feed and in many industries as adhesives, emulsions, cleansing materials, pharmaceuticals, inks, plastics and also textile fibres. Raw material for spinning textile fibres is obtained from soybean remaining flakes after the extraction of oils and other fatty substances (Li, 2004).

Amino acids content of soybean proteins is given in Fig. 2. Soybean proteins contain 18 different amino acids. There are about 23% of acidic amino acids (glutamic acid and aspartic

amino acid), about 25% of alkaline amino acids (serine, arginine, lysine, tyrosine, threonine, tryptophan) and about 30% of neutral amino acids (leucine, phenylalanine, valine, alanine, isoleucine, proline, glycine). Sulphur containing amino acids are present also in soy proteins: about 1.0% of cysteine and 0.35% of methionine.

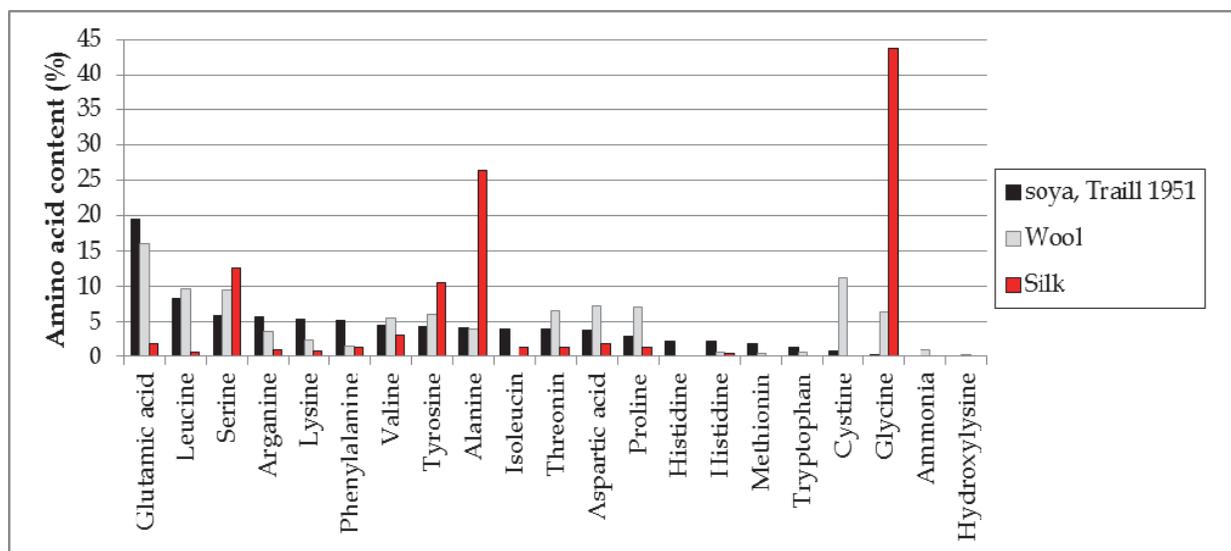


Fig. 2. Amino acids content in soybean proteins, wool keratin and silk fibroin (Brooks, 2005).

Soybean proteins consist of various groups of polypeptides with a broad range of molecular size: about 90% are salt-soluble globulins (soluble in dilute salt solutions) and the remainder is water-soluble albumins (Zhang, 2008). Very important as raw material for producing textile fibres are storage globulins with predominant β -conglycinin (30–50% of the total seed proteins) and glycinin (ca. 30% of the total seed proteins). β -conglycinin is a heterogeneous glycoprotein composed of three subunits (α' , α , β) contained asparagine, glutamine, arginine and leucine amino acids. Subunits are non-covalently associated into trimeric proteins by hydrophobic interactions and hydrogen bonding without any disulphide bonds. Glycinin is a large hexamer, composed from acidic and basic polypeptides linked together by disulphide bonds (Zhang, 2008). On the basis of the sedimentation coefficient, a typical ultracentrifuge pattern of soybean proteins has four major fractions: 2S, 7S, 11S, and 15S (Zhang, 2008).

Globular proteins are composed of segments of polypeptides connected with hydrogen bonds, electrostatic interactions, disulphide bonds and hydrophobic interactions. Conformational changes of unfolding globular proteins through denaturation process (Zhang & Zeng, 2008) and reducing the inclination of denaturated proteins to form aggregates are important for spinnability of a spinning dope with proper relative viscosity. It is also important for later drawing of fibres and crystallization of proteins in fibres. Denaturation (Fig. 3) is modification of the secondary, tertiary, and quaternary structure of protein. Exposure of soybean proteins to strong alkali/acids, heat, organic solvents, detergents and urea causes the denaturation of native globular proteins, i.e. converting into unfolded polypeptide chains, which are connected with interchanging of disulphide bonds. Extruded fibres coagulate in a precipitation acid bath and new disulphide bonds are formed. The structure of soybean proteins and changes at converting globular proteins into fibre forming proteins are given in Fig 3.

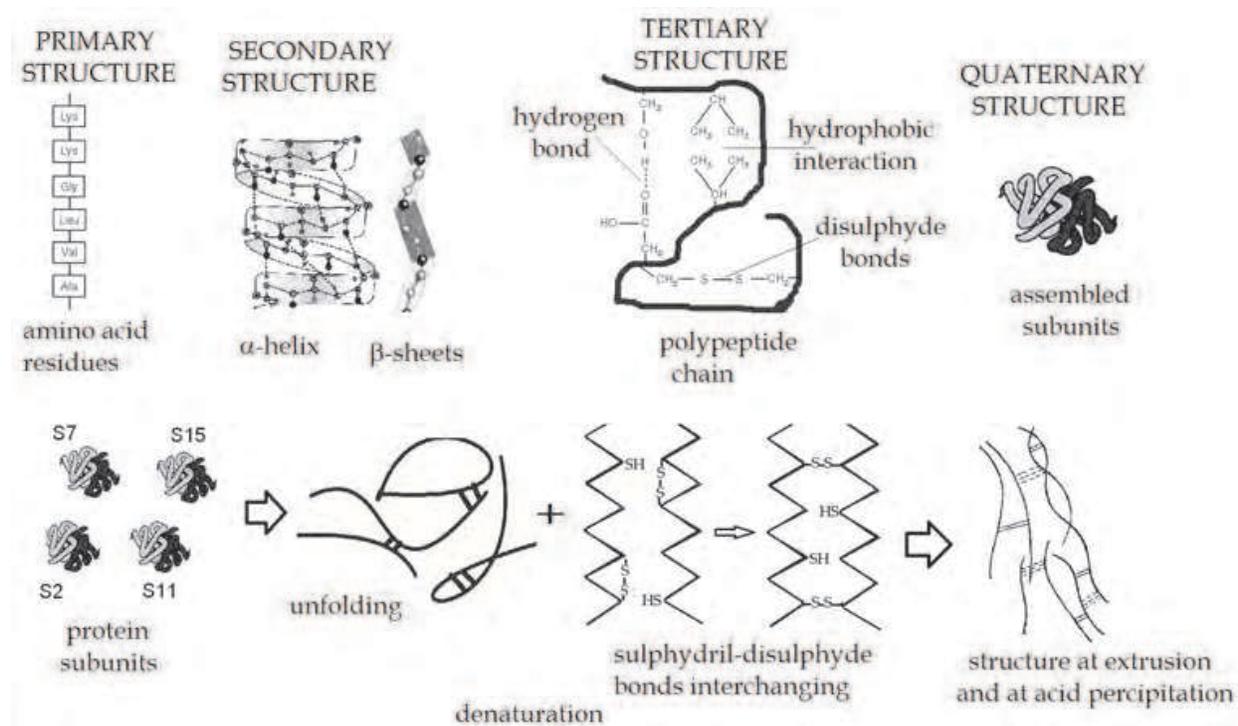


Fig. 3. Protein levels and conversion of globular proteins into fibre forming proteins (Zhang & Zeng, 2008; Kelly & Pressley, 1996).

Oils extraction with solvents used in the mid-twentieth century, was critical for the whole spinning process of soybean fibres, because the chosen temperatures, pH, urea, salts, organic solvents (hexane) and reducing agents influence on the degree of denaturation of proteins, degradation of proteins and changing of proteins colour. Protein degradation is detrimental to the production of high-strength protein fibres. Modern method of modifying soybean globular proteins is biochemical with using enzymes and auxiliary agent (Swicofil, 2011).

2.2 Pure soybean protein fibres from the mid-twentieth century

First researches for developing fibres from soybean proteins were made by the Japanese. In the year 1940 the first US patent was granted to Japanese Toshiji Kajita and Ryohei Inoue (Kajita & Inoue, 1940). The oil-free protein substance was extracted with dilute alkaline solution and precipitated by adding metallic salts. The protein was then washed in water and added by tartaric acid when the precipitate was wet. Then it was again dissolved in alkaline solution to form a spinning dope. Fibres were spun in an acid bath with organic coagulating agent (alcohol, formaldehyde, acetone etc.), where filaments hardened (Kajita & Inoue, 1946). The fibres had natural white to light tan colour. They were crimped, with high resiliency, warmth and soft feel. In comparison to wool they had lower tensile strength, especially in wet state, and lower moisture absorbency.

Patents for spinning fibres from soybean proteins were granted to the American Oscar Huppert from Glidden Company (Huppert, 1945) and Robert A. Boyer from Ford Motor Company (Boyer et al., 1945). In 1939 the American Ford Motor Company produced soybean protein fibres for their car's upholstery and seats fillings. The fibres, which have never been commercialized, had about 80% the strength of wool, higher elongation in dry and wet state than wool and didn't wet so easily as wool or casein fibres (Boyer, 1940).

Chemical and dyeing properties of pure regenerated soybean protein fibres were similar to wool.

Soybean protein fibres were also produced in Japan under the name Silkool (Myers, 1993). In 1939 the fibre production reached about 450–1,200 tons.

Low tensile strength of soybean protein fibres in wet state limited their commercial application. Fibres were used predominantly in blends with wool, cotton or synthetic fibres in woven and knitted fabrics for apparel and in upholstery, also in cars, despite of lower abrasion resistance than wool (Fletcher, 1942). The production of the mid-twentieth soybean protein fibres was ceased at the end of the World War II.

2.3 Researches on soybean protein fibres in the early twenty-first century

Huang et al. (1995) have made experimentally the textile fibres from soybean protein by re-examining the wet spinning method, described in the literature (Croston et al., 1945). The properties of the fibres made by wet spinning method from alkaline solution of soybean protein isolate and coagulated in acid bath were compared with the fibres made by dry spinning method of water solution of soybean protein isolate. Tensile properties of treated fibres were 0.77 cN/dtex at 11% relative humidity (r.h.), 0.75 cN/dtex at 65% r.h. and only 0.08 cN/dtex in wet state. They were lower than those of wool in most conditions (Huang et al., 1995). They found out that dry spinning was a suitable method for spinning soybean protein fibres because of their good solubility in water and glycerol. In the next experimental step they tried to increase tensile properties by decreasing the moisture absorption of soybean protein fibres. They used relatively nonpolar zein proteins (20, 30 and 40%), which were added to soybean protein into the spinning dope. Fibres were made by dry spinning method. The optimum soy protein-zein blended fibre was made from a suspension containing 80% of soybean protein and 20% of zein in glycerol (Zhang et al., 1997), but the tenacity was only 0.20 cN/dtex.

Another idea to improve low tensile strength and decrease shrinkage in boiling water was using water-soluble polymer, such as polyvinyl alcohol (PVA). PVA fibres are produced in similar conditions as phytoprotein fibres. Zhang (Zhang et al., 1999) experimented with bicomponent fibres from soybean protein and PVA. Fibres with a side-by-side configuration were not successful because of splitting of the components. The reason was in too large difference in swelling of the components in water. The next experiment of spinning sheath-core bicomponent fibres, with PVA component in the sheath and soybean proteins in the core, showed brittle core that couldn't be drawn. „The degradation of the soybean protein and the existing microgels in the protein spinning solution were thought to be the causes for the poor fibre drawability“ (Zhang et al., 1999).

After ten years of intensive researches the Chinese scientists with Guanqi Li succeeded in producing high-tenacity soybean protein fibres from soybean protein and polyvinyl alcohol (Li, 2007). The process and fibre's properties are presented in section 2.4. Polyvinyl alcohol adds strength and acceptable wearability characteristics to the new SPF.

Biconstituent fibres from a biocompatible soy protein isolate and cellulose were produced experimentally from new aqueous solution NaOH/thiourea/urea. Strong hydrogen bonds between hydroxyl groups of cellulose and amid groups of protein were formed. Fibres with linear density of 6.2 dtex were produced with tensile strength of 1.86 cN/dtex and breaking elongation of 10.3% (Zhang et al., 2009).

High-wet strength fibres containing 5–23% of a soybean protein isolate from oiled soybean cake and 77–95% of polyvinyl alcohol were developed by scientists with Guanqi Li at

Huakang R&D Center in China (Li, 2003, 2007). A soybean protein isolate is treated with an auxiliary agent and biological enzymes to modify the structure of globular proteins. Additives break the disulphide bonds in globular proteins and convert them into linear molecules, which are stable in temperature range 55–90 °C (Mathur & Hira, 2004).

Fibres are wet spun from deaerated spinning dope composed of a soybean protein and polyvinyl alcohol dissolved in distilled water, followed by adding of borax or boric acid and mixing at temperature between 40 and 98 °C. After coagulation in a water bath with salt and alkali, as spun fibres are wet drawn, then dried, pre-heat set, heat-set at 170–185 °C, cooled, wound, stabilised by acetalysing, washed, oiled, crimped and cut into staple fibres. Production process doesn't pollute the environment. Most added agents in the process can be recovered from semi-finished fibres and used again.

The molecules of protein are laterally bonded with molecules of polyvinyl alcohol in the fibres. This enables during additional extension, orientation and crystallisation of proteins in the fibres during drawing. The morphological structure of SPF consists of less oriented sheath and well oriented microfibrillar core. The fibres have about 10% of hydrophilic groups in amorphous regions (Mathur & Hira, 2004).

Properties of soybean protein fibres taken from yarn SoySilk™ and milk protein fibres taken from yarn SilkLatte® are given in Table 1 (Brinsko, K. M., 2010).

Yarns	soybean protein fibres	milk protein fibres
available from	Southwest Trading Company	Southwest Trading Company, Tempe, AZ
cross-section and longitudinal view	bean-shaped with pronounced and elongated micro-pores inclusions	bean-shaped with small micro-pores inclusions
birefringence	0.021–0.027	0.016–0.024
melting point	250–260	235–245
chloroform, AcOH, acetone, DMF	insoluble	insoluble
formic acid	swell	swell
conc. H ₂ SO ₄ , conc. HNO ₃	partially soluble	soluble, gels
characteristic peaks on FT-IR spectrum	amide I at 1640 cm ⁻¹ amide II at 1530 cm ⁻¹	amide I at 1640 cm ⁻¹ amide II at 1530 cm ⁻¹

Table 1. Properties of soybean protein fibres taken from yarn SoySilk™ and milk protein fibres taken from yarn SilkLatte® (Brinsko, K. M., 2010).

Adding some metallic salts into spinning dope, endows soybean fibre with far-infrared, negative ion and anti-bacterial functions. Only 3% of such fibres added into yarn can give stable and permanent antibacterial effect. Another technology from the same university is adopting ZnSO₄ as the dehydrating agent for soybean fibre spinning. In the course of after-processing, ZnSO₄ reacts with NaOH, forming ZnOH, which after drying is deoxidized into nanograde ZnO that can form covalent bond with fibre itself, taking a strong screen effect to ultraviolet radiation (Yang, 2011).

2.4 Commercial soybean protein fibres in the early twenty-first century

SPF based on the Li Guanqi patent (Li, 2007) are the first industrially produced fibres from soybean proteins in the world and they are the only soybean protein fibres present on the

market today. These fibres are also the first manufactured fibres, developed by China. The production process of the new SPF was laboratory established in 1993 and commercially promoted in 2000. In 2001 the fibres were standardised and in 2003 launched.

About 1,500 tons of the fibres per year are produced under the brand name Winshow by Shanghai Winshow Soybean Fibre Industry Co., Ltd. Six manufacturing bases were established in four provinces in China for producing SPF (Shanghai, 2011). Zhejiang Jiali Protein Fiber Co., Ltd. is the owner of the soybean protein fiber international intellectual property rights and production line.

The Chinese manufacturer of soybean protein fibres Harvest SPF Textile Co., Ltd. (www.spftex.com) is a Chinese-foreign joint venture co-incorporated by China Harvest International Industry Ltd. and Zhejiang Jiali Protein Fiber Co. Ltd. (Shanghai, 2011). They are specialized in the research and development of new textile fibre raw material application technologies and application of the new-type textile materials from SPF. Fibres and yarns from soybean protein fibres are also available from Swicofil AG Textile Service (Anon, 2011), South West Trading Company with yarn SoySilk™ (SWTC, 2011).

Since SPF resemble in their softness and shine to silk and cashmere, producers market them as "artificial cashmere", "vegetable cashmere" or "soy silk" fibres to partially decrease needs for natural silk and cashmere fibres. Cashmere goats cause damages to lands, so reducing their number has ecological benefits.

Physical and chemical properties of soybean protein fibres are given in Table 2.

PROPERTIES	SPF	Cotton	Viscose	Silk	Wool
Breaking strength (cN/dtex) in dry state	3.8–4.0	1.9–3.1	1.5–2.0	2.6–3.5	0.9–1.6
Breaking strength (cN/dtex) in wet state	2.5–3.0	2.2–3.1	0.7–1.1	1.9–2.5	0.7–1.3
Breaking elongation (%) in dry state	18–21	7–10	18–24	14–25	25–35
Initial Modulus (kg/mm ²)	700–1300	850–1200	850–1150	650–1250	
Loop strength (%)	75–85	70	30–65	60–80	
Knot strength (%)	85	92–100	45–60	80–85	
Moisture regain (%)	8.6	9.0	13.0	11.0	14–16
Density (g/cm ³)	1.29	1.50–1.54	1.46–1.52	1.34–1.38	1.33
Heat resistance	Yellowing and tackifying at about 120 °C (Bad)	Becoming brown after long time processing at 150 °C (Excellent)	Strength down after longtime processing at 150 °C (Good)	Keep stable when temperature ≤148 °C (Good)	(Good)
Alkali resistance	At general level	Excellent	Excellent	Good	Bad
Acid resistance	Excellent	Bad	Bad	Excellent	Excellent
Ultraviolet resistance	Good	At the general level	Bad	Bad	Bad

Table 2. Comparison of physical and chemical properties of soybean protein fibres (SPF) in comparison to cotton, viscose, silk and wool (Swicofil, 2011).

A raw SPF has light yellow colour, like silk oak. Before dyeing into light colours they should be bleached with hydrogen peroxide or reduction bleached. SPF fibres can be dyed at temperatures lower than 100 °C with weak-acid dyes and substantive dyes for very few colours, because the dyeing fastness is poor. As SPF are less sensitive to high pH, they could be also dyed with reactive dyes (Mathur & Hira, 2004). SPF fibres have good light fastness and good resistance to ultraviolet radiation, which is better than that of cotton, viscose and silk. They are stable to washing even at higher temperatures, but they yellow at dry heat at 120–160°C (Anon., 2003).

Likewise regenerated cellulose bamboo fibres, SPF fibres are promoted on the market as biocompatible and health giving with natural antibacterial properties. The Chinese herbal medicine with sterilising and anti-inflammatory properties can be bonded on side chains of the proteins during the production of SPF (Yi-you, 2004) due to the bacterial resistance of SPF fibres to *Styphalococcus aureuses*, *coli bacillus* and *Candica albicans* (Swicofil, 2011). Mathur has mentioned that SPF resistance to golden and yellow *Styphalococcus aureuses* is more than 5.8 and hence they are inherently anti-bacterial fibres (Mathur & Hira, 2004).

Beside in yarns from 100% of SPF, the SPF cotton type fibres could be used in yarn mixtures with cotton, polyester, viscose and bamboo viscose. The wool type SPF should be mixed with cashmere (80/20 SPF/cashmere), lyocell, silk or wool (50/50 SPF/wool). Smooth surface of SPF has influence on low spinnability because of low friction coefficient and low cohesion force, and on pilling.

Fabrics with SPF should not be mercerised because SPF are not resistant to strong caustic soda. Woven and knitted fabrics can be used for apparel (personal underwear, T-shirts, pullovers, sweaters, evening dresses, children's clothing and sportswear) and home textiles (towels, bed linen, blankets, bathrobes, pyjamas). Since the fibres have lower abrasion resistance than wool they can be used as upholstery in automobile textiles.

A cloth made of SPF fibres exhibits good wiping properties (Reek, 2008). At least 10% of Winshow SPF of linear density 1.5 dtex and 38 mm length from Shanghai Winshow Soybeanfibre Industry Co., Ltd. of Shanghai, China is used in combination with viscose and/or other textile fibres in thermo-bonded nonwoven fibrous material.

2.5 Biodegradation of contemporary SPF

Biodegradable fibres degrade relatively quickly through biological process, which depends on many factors, such as chemical and morphological structure, temperature, pH, relative humidity and remains of auxiliary agents, which are accumulated (brought) on fibres during manufacturing and are not completely washed after finishing process (Simončič & Tomšič, 2010).

The chemical structure has influence on biodegradability with its hydrophilic nature (wettability), crystallinity of the polymer, chemical linkages in the polymer backbone, pendant groups, end groups and molecular weight distribution. Peptide bonds are susceptible to enzymatic degradation. Additional polymers may (interaction with other polymers) act as barriers to prevent migration of microorganisms, enzymes, moisture or oxygen into the polymer domain of interest (Zee, 2005).

The biodegradation process of proteins is initiated through exposure to water. Long macromolecules under hydrolytic process convert into many small molecules, which are more proper for the metabolism of microorganisms.

The mid-twentieth pure soybean protein fibres mildewed less easily than natural and casein fibres but more easily than synthetic fibres (Fletcher, 1942). Mid-twenty century soybean

protein fibres were susceptible to microbiological growth. Casein fibres were readily damaged by mildew, they quickly mildewing especially in damp conditions. Changing protein molecules by chemicals and tanning (hardening) has influence on lower biodegradability of fibres (Wormell, 1954).

Very little data is yet available about biodegradability of contemporary soybean protein fibres. The fibres are promoted as biodegradable fibres in landfill (Mathur & Hira, 2004; Swicofil, 2011). Fibres from water-soluble polyvinyl alcohol are biodegradable in soil. Considering the chemical structure of SPF (Fig. 2), the soybean proteins susceptibility to biodegradation should be similar to wool and not to silk. Wool contains 80% of keratin, the rest are no-keratin proteins. Degradation of wool is mostly caused by fungus and less by bacteria. Ideal conditions for growth of microorganisms on wool fibres are temperature 30°C, relative humidity of 95% and pH from 6,5 to 8,5 (Edwards & Vigo, 2001). In the initial stage, of biodegradation of wool is hard to be noticed. When the growth of microorganisms increases, unpleasant odour appears, coloured spots can be seen on fabrics and tensile strength as result of defibrillation decreases (Edwards & Vigo, 2001, Szostak-Kotowa, 2004).

3. Experimental part

3.1 Materials

Ring spun yarns and twill 2/2 woven fabrics were used in our experiments of biodegradation of contemporary soybean protein fibres:

- 100% soybean protein yarn with linear density of 15 tex (SPF yarn) and 100% cotton yarn with linear density of 19 tex for comparison;
- a fabric with yarn from soybean protein fibres in weft direction and cotton yarn in warp direction (SPF/CO) and a 100% cotton fabric with cotton yarn in warp and weft direction for comparison (CO).

The same cotton yarn with linear density of 28 tex were used for warp and SPF yarn with linear density of 15 tex were used for weft for all woven fabrics. The density of fabrics was 30 ends/cm and 28 picks/cm for SPF/CO and 100% cotton fabrics.

3.2 Methods

3.2.1 Method of controlled biodegradation in soil

A laboratory experiment of biodegradation (Fig. 4) of yarns and woven fabrics was made in accordance with the standardised method SIST EN ISO 11721-1. Commercial humus, rich in microorganisms, was used as a soil. During experiment the soil humidity was 60±5%, which was regularly measured by a hygrometer and maintained by spraying the soil with tap water. The temperature of the soil was 25–30 °C. Samples of yarns and woven fabrics were buried in the soil for 2, 7, 11, 16 and 21 days. After that, the samples were washed out in tap water, then immersed into ethanol for 30 minutes to stop the activity of microorganisms, and dried in the air.

Tensile properties of samples were measured on dynamometer Instron 5567 in accordance with the standard SIST EN ISO 2062 for yarns and SIST EN ISO 13934 for fabrics. For measuring tensile properties in wet state, the yarns were immersed into distilled water with detergent at room temperature for an hour. Tensile properties of yarns were analysed with the DINARA program (Bukošek, 1988). Tensile properties of fabrics were measured only in weft direction.

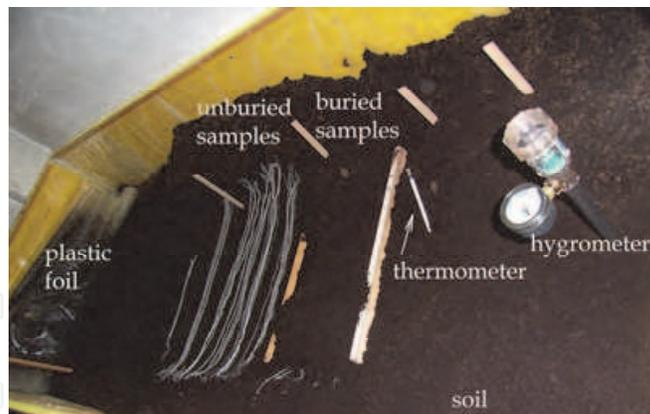


Fig. 4. Experiments of biodegradation were made in a wooden box surrounded with a foil and filled with humus soil.

3.2.2 Other methods

Fourier transform infrared spectra (FTIR/ATR) were obtained on the Spectrum GX (Perkin Elmer) with the Michelson interferometer and Spectrum 5.01 software using 16 scans at a resolution of 4 cm^{-1} in a range of wavenumber from 4000 to 500 cm^{-1} . Microphotographs were made with the Jeol JSM 6060 LV scanning electron microscope and the Nikon SMZ 800 stereomicroscope.

4. Results and discussion

4.1 Fibres properties

The SPF yarn was made from cotton type soybean fibres of 1.27 dtex with an average length of 39.5 cm . Fibres were thermoplastic with melting point at 224°C . Dry fibres absorbed 2.47% of moisture when exposed for 48 hours to the air of relative humidity 50% and temperature of 23°C .

The cross-section shape of used soybean protein fibres was bean-shaped with diameter of $11\text{-}20\ \mu\text{m}$ in longer axle and $6\text{-}7\ \mu\text{m}$ in shorter axle (Fig. 5). A very smooth surface of fibres imparted high lustre to fibres. On the longitudinal view irregular grooves and wrinkles can be seen. These grooves can help to transport moisture along fibres. On the optical microscope photograph a nonhomogeneous structure with many voids is seen.

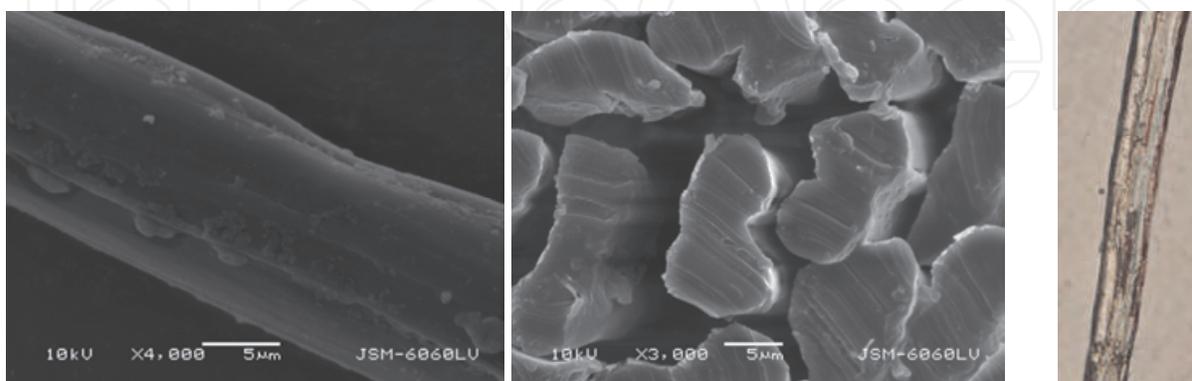


Fig. 5. Scanning electron microscope view of soybean protein fibre: top: longitudinal view at magnification of 4.000 and bottom: cross-section at magnification of 3.000 . Right: optical microscope longitudinal view of soybean protein fibre.

Soybean protein fibres are composed of a mixture of two polymers, soybean proteins and polyvinyl alcohol. Protein and polyvinyl alcohol macromolecules are connected by intermolecular interactions like hydrogen bonds (Fig. 3) and van der Waals hydrophilic and hydrophobic forces.

The soybean protein fibres, used in experiment, consisted of polyvinyl alcohol and soybean proteins. The SPF FT-IR spectrum (Fig. 6) has very intensive peaks at 3301 cm^{-1} , which is typical for stretching O-H bonds, and at 1408 cm^{-1} and 1327 cm^{-1} , which corresponds to N-H stretching in amide III. FT-IR absorption spectrum of SPF is different to FT-IR spectrum of PVA fibres at peaks 1644 cm^{-1} and 1535.32 cm^{-1} .

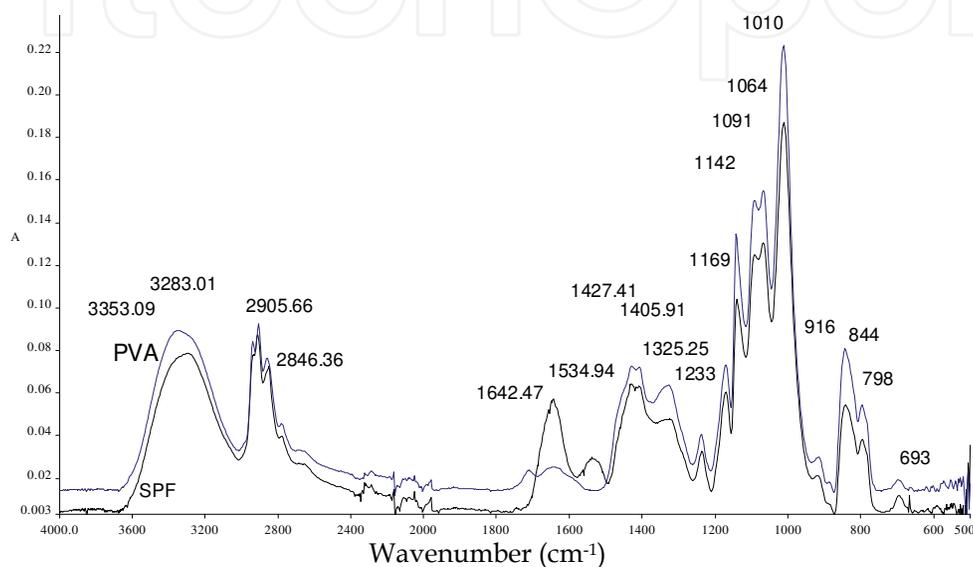


Fig. 6. FT-IR/ATR absorption spectra of soybean protein fibres (SPF) and PVA Kuralon®.

Pure soybean protein isolate has typical infrared absorption bands at $1636\text{--}1680\text{ cm}^{-1}$ and $1533\text{--}1559\text{ cm}^{-1}$ that are attributable to the -NH- bonds of amide I at 1640 cm^{-1} and at 1550 cm^{-1} for amide II in peptide bonds forming primary backbone of proteins. The absorption peak at 3294 cm^{-1} refers to the hydrogen-bond association between protein chains and moisture in protein. The absorption band at $1241\text{--}1472\text{ cm}^{-1}$ is attributable to the (C)O-O and C-N stretching and N-H bending (amide III) vibrations (Su et al., 2008).

At room temperature pure polyvinyl alcohol powder with -OH groups on carbon chains has a typical infrared absorption band at $2918\text{--}3565\text{ cm}^{-1}$, which corresponds to -OH absorption (Su et al., 2008).

4.2 Yarns properties

4.2.1 Tensile properties of SPF yarn in dry and wet state

Water has a significant influence on tensile properties of the SPF yarn (Fig. 7, Tab. 3). After an hour in distilled water, the yarn lost its specific breaking stress for almost one third. Wet yarn had lower modulus than dry yarn in the whole deformation range and attained by 11.4% higher breaking elongation than dry yarn.

4.2.2 Biodegradation of SPF yarns

Biodegradation of SPF yarn was studied after the yarn had been buried for 2, 7, 11, 16 and 21 days in the soil with temperature about $30\text{ }^{\circ}\text{C}$ and 65% relative humidity (Fig. 8). For the

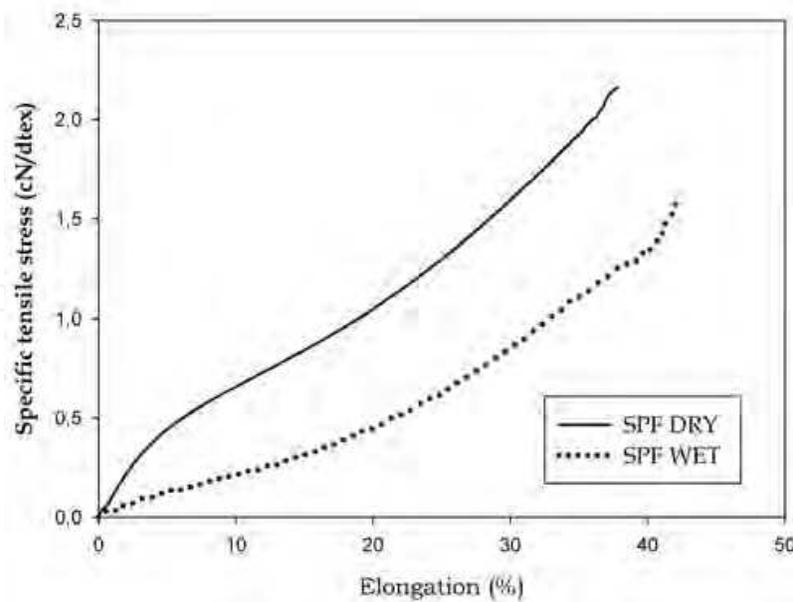


Fig. 7. Stress-elongation curves of dry and wet SPF yarns

Properties of yarns from SPF	DRY	WET	Δ (%)
Specific breaking stress (cN/dtex)	2.16	1.58	-26.9
Breaking elongation (%)	37.75	42.05	+11.4
Initial modulus (GPa)	5.08	3.25	-36.0
Specific work of rupture (mJ/kg)	39.81	22.71	-43.0

Table 3. Tensile properties of dry and wet SPF yarns and relative differences between them (Δ).

purpose of comparison, cotton yarn was buried at the same time in the soil. After 7 days cotton yarn degraded very intensively and only small remains of yarn were left in the soil. Tensile properties of biodegraded cotton yarn could be measured only after 2 days. Biodegradation of cotton showed that microorganisms in the soil were active during the experiment.

The microphotographs of SPF yarns in Fig. 8 show that the quantity of bacteria and fungus, present on the surface of soybean protein fibres, increased with time of biodegradation. After 21 days in the soil, it is hard to say that there are any physical degradations of the fibre's surface because the fibres have natural irregular grooves and wrinkles (0 days).

Soybean protein fibres in comparison to the mid-twentieth century protein fibres (Fig. 1) have essentially smoother surface and relatively lower quantity of surface grooves that could enable bacteria to penetrate into the fibres.

Specific tensile stress-elongation curves of biodegraded cotton yarns (Fig. 9 and 10) show a significant decrease of breaking force and breaking elongation after 2 days, while for the yarns from soya protein fibres, they didn't change essentially.

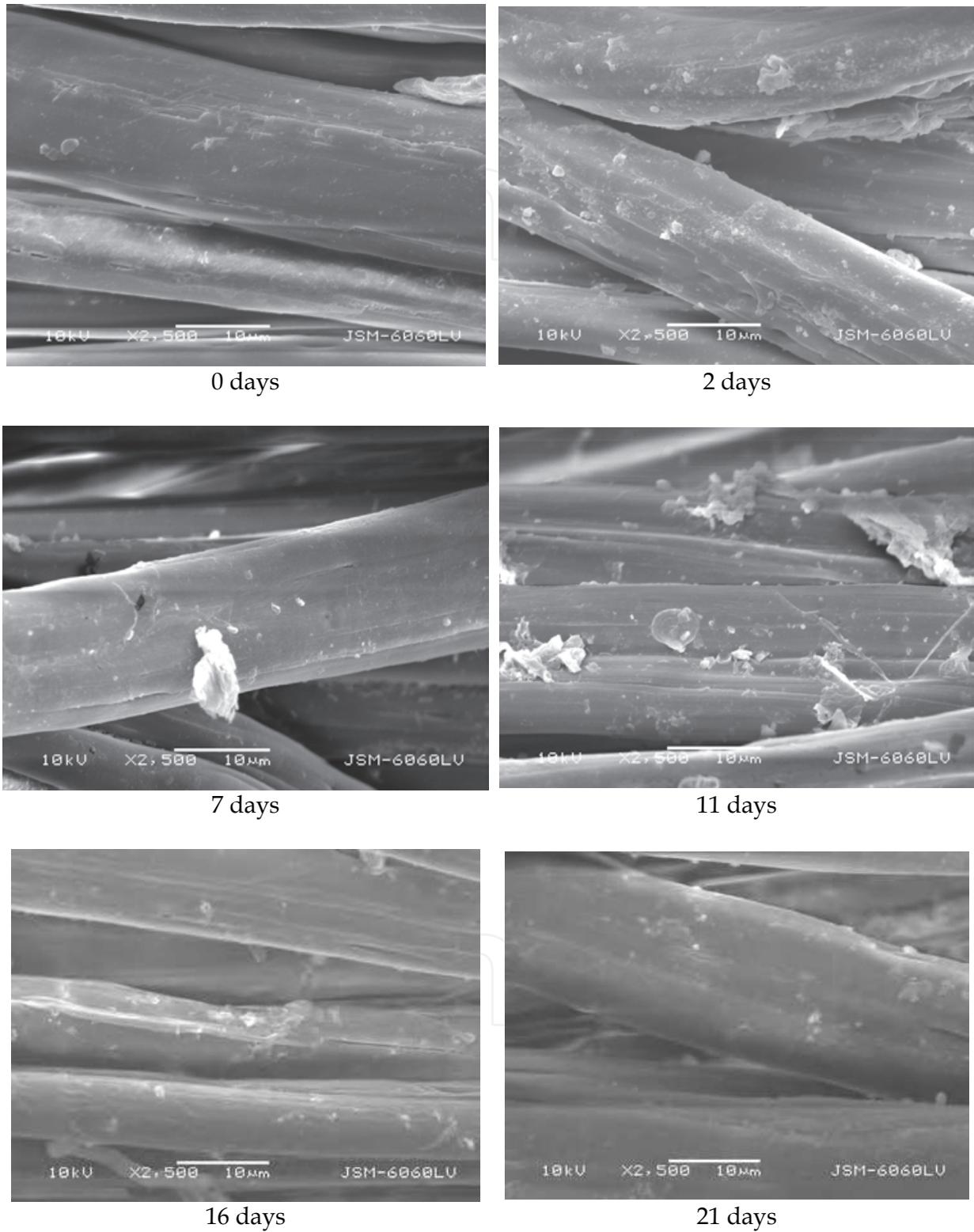


Fig. 8. SEM microphotographs of SPF yarns after having been buried for 0, 2, 7, 11, 16 and 21 days in the soil (at magnification 2500-x).

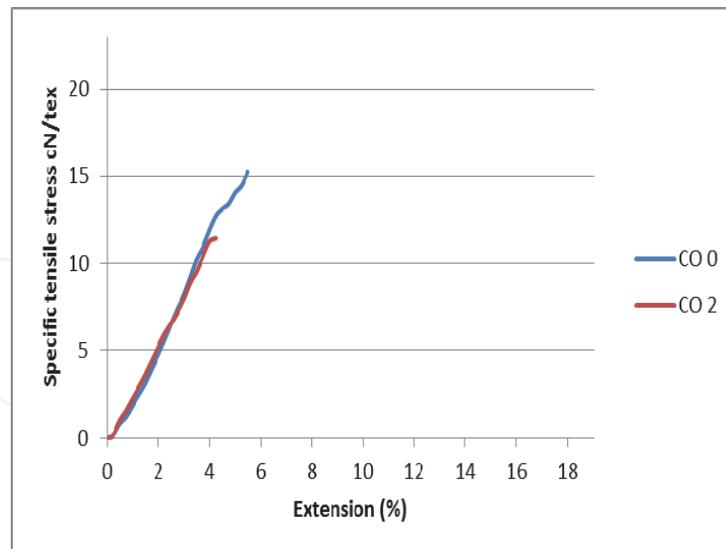


Fig. 9. Stress-elongation curves of cotton yarns after having been buried for 0 (CO 0) and 2 (CO 2) days in the soil.

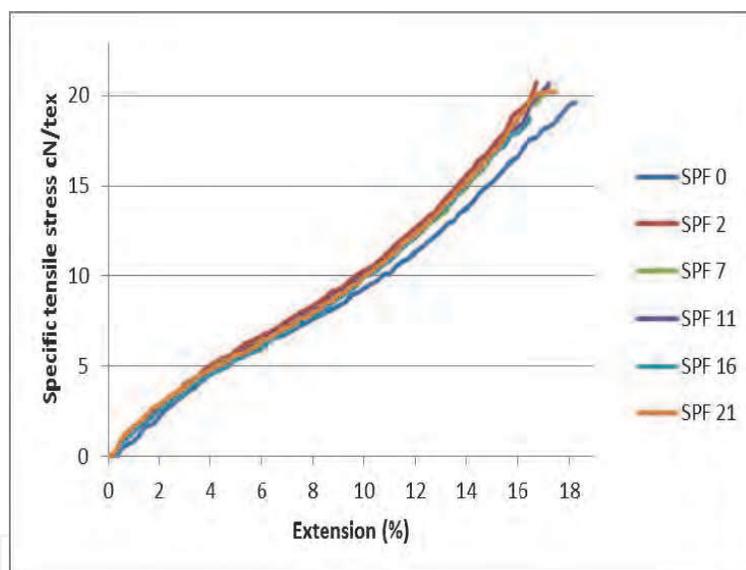


Fig. 10. Stress-elongation curves of cotton yarns after having been buried for 0 (SPF 0) to 21 (SPF 21) days in the soil.

4.3 Biodegradation of fabrics with SPF yarns in weft direction

Woven fabrics were buried at the same time as yarns into the soil at temperature 30°C and relative humidity 65% for 2, 7, 11, 16 and 21 days. Fabric samples (Fig. 11) changed the colour and became browner with many colour spots on the surface, which confirmed the existence of fungus.

Pure cotton fabrics degraded in one weak to such degree that they broke up into pieces when we tried to dig them out of the soil. After 21 days only very little remains were found in the soil. Fabrics with yarns from soybean protein fibres in weft direction were more compact in weft direction than pure cotton fabrics. But in warp direction from cotton yarns the fabrics lost their strength and were easily torn (Fig. 11).

Fig. 12 shows that after 21 days in the soil the cotton cuticle was destroyed. On the soybean protein fibres the quantity of fungus and bacteria increased, but the surface of fibres was not damaged.



Fig. 11. Fabric samples after having been buried in the soil for 0 to 21 days. (Photo: Marica Starešinič)

The longer was the time of being buried in the soil, the greater was the loss of tensile strength of cotton fabrics: by 12% after 2 days and by 62% after 7 days of being buried in the soil. Breaking elongation decreased also rapidly: from 23% of the unburied fabric to only 8% after 7 days of being buried in the soil (Fig. 13).

Degradation of cotton yarns in warp direction affected tensile strength of SPF/CO fabrics in weft direction (Fig. 14). Fabrics buried in the soil for 7 days lost 12% of their tensile force, but after 21 days of being buried in the soil their breaking force decreased by additional 13% in comparison to unburied fabrics. Breaking elongation in weft direction of SPF/CO fabrics did not change significantly.

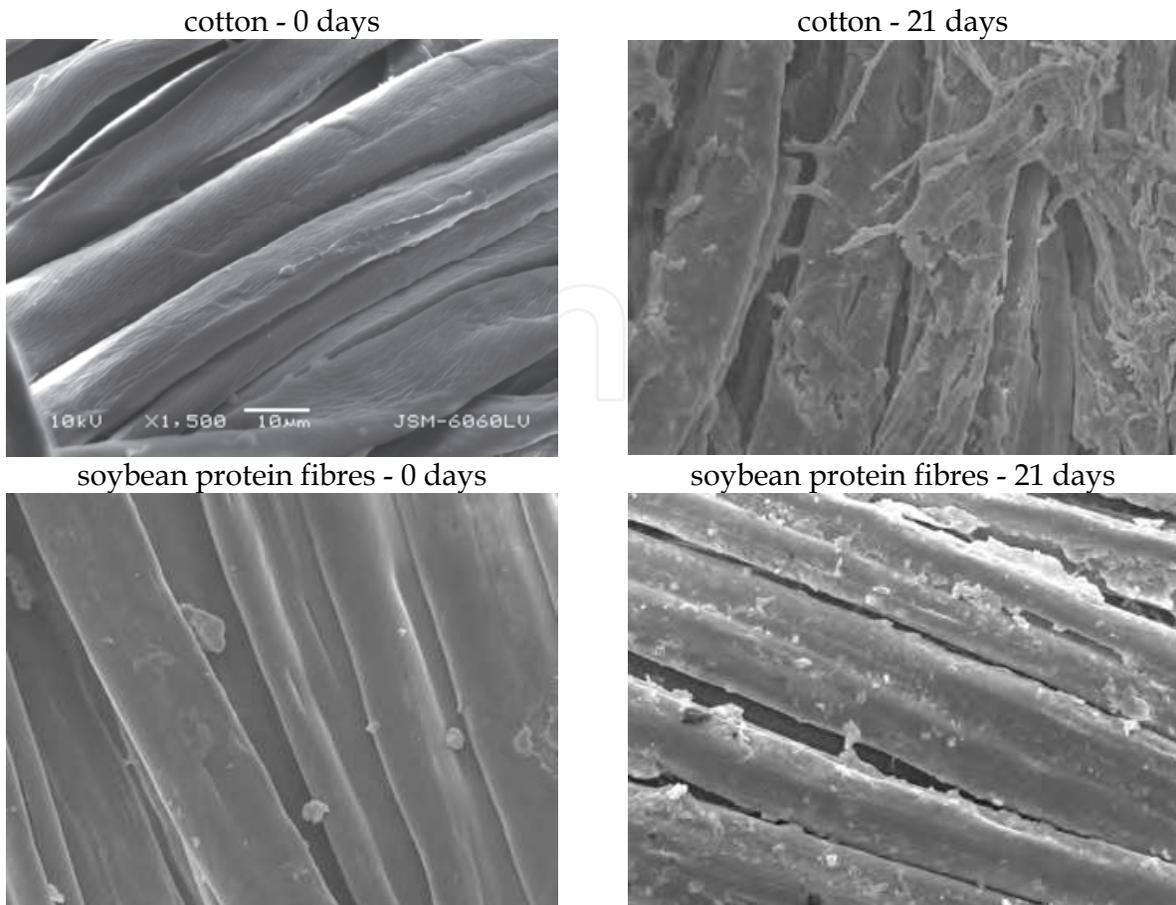


Fig. 12. SEM microphotographs of CO fabrics and SPF/CO woven fabrics (magnification 1500-x).

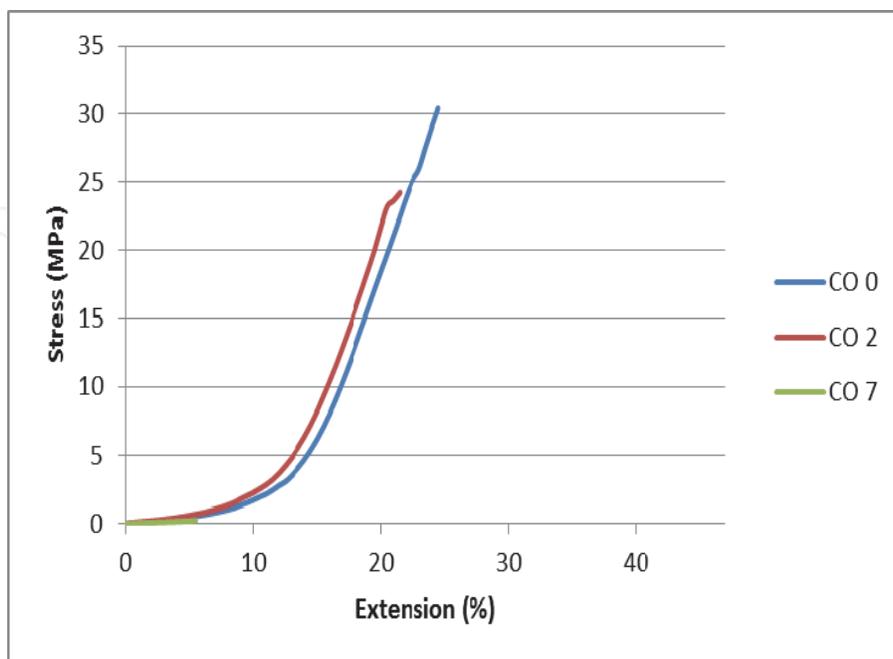


Fig. 13. Stress-elongation curves for cotton woven fabrics.

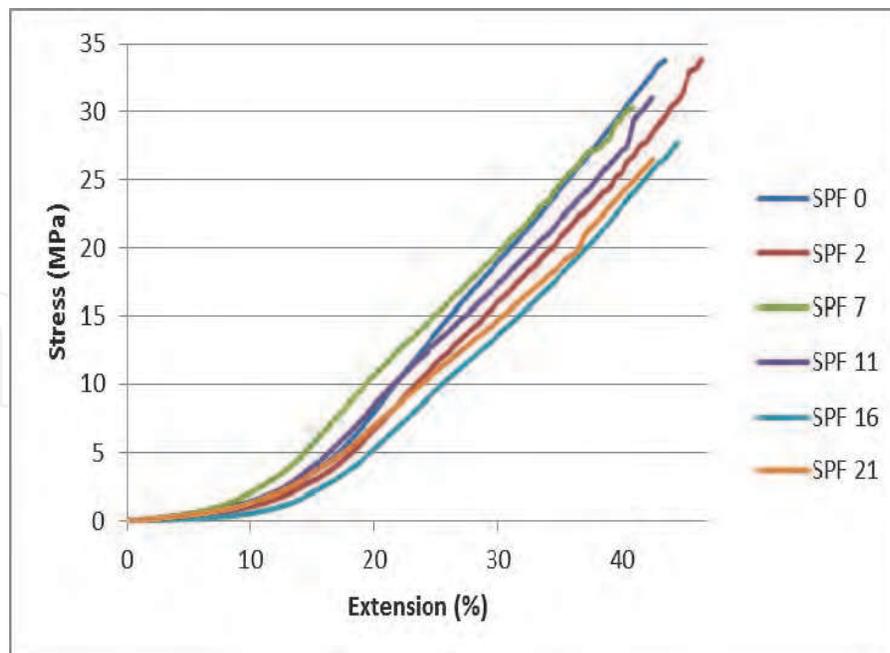


Fig. 14. Stress-elongation curves for woven fabrics with SPF yarn in weft.

5. Conclusion

The mid-twentieth century regenerated soybean protein fibres were made from pure soy proteins treated with formaldehyde or aluminium salts. Because of low tensile strength in wet state they were, like all other mid-twentieth protein fibres, noncompetitive to synthetic fibres in the 1970th.

Due to increasing prices of petroleum and a growing concern about the environmental damage arising from a slow degradation and poor biodegradability of synthetic fibres, researchers began to search for new possibilities of developing fibres from renewable raw materials, also from soybean proteins.

The fact that proteins are renewable and biodegradable materials has attracted considerable attention of many researchers in the area of textile fibres in the last two decades to re-examine the production of fibres from soybean proteins and casein. Soybean proteins have a greater potential for use as textile fibres because of their lower cost than casein proteins derived from milk.

In all experiments made until now, a soybean protein isolate (SPI) has been used, which is a highly purified protein (>90% w/w), obtained after extracting oils and fats from protein cakes. The residues after purification of protein for producing fibres can be also used as foodstuff (Yi-you, 2004).

In the last two decades researches have focused on different spinning methods (Huang et al., 1995), on new fibres from soybean proteins and polyvinyl alcohol (Zhang et. al., 1999, Li, 2007) or zein proteins (Zhang et al., 1997), on new economical biochemical processes that modify physical structure of soya proteins, and on new solvents (Zhang et al., 2009).

The experimental soybean protein fibres were made from two macromolecular components combined together into:

- *biconstituent fibres*, where a spinning dope was prepared from a homogeneous mixture of two solutions - a soybean protein water solution and a water solution of synthetic

polymer polyvinyl alcohol or cellulose or zein proteins. Single fibres made from such spinning dopes had homogenous structure.

- *bicomponent fibres*, where the fibre's core was made from a soybean protein and the fibre's sheath from polyvinyl alcohol.

Polyvinyl alcohol was used, because it is a water-soluble polymer, it dissolves at similar conditions as proteins and when added to proteins, it increases the fibre's strength. Polyvinyl alcohol is also biodegradable in the soil (Brooks, 2005).

The combination of cotton yarns and the yarns from soybean proteins in woven fabrics imparts comfort, soft hand and good moisture absorption properties to undergarments, outerwear, infants' wear, towels and beddings. Biodegradation of contemporary soybean protein fibres in early phase, up to 21 days in the soil at 30 °C and 65% relative humidity, is a slow, hardly perceivable process.

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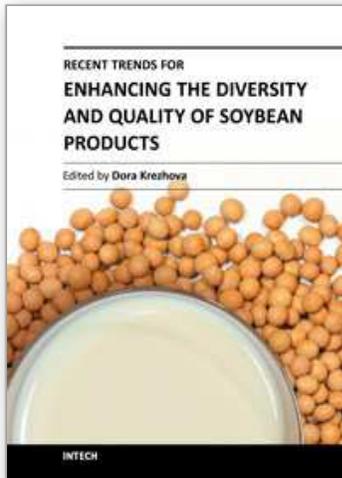
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This book presents new aspects and technologies for the applicability of soybean and soybean products in industry (human food, livestock feed, oil and biodiesel production, textile, medicine) as well as for future uses of some soybean sub-products. The contributions are organized in two sections considering soybean in aspects of food, nutrition and health and modern processing technologies. Each of the sections covers a wide range of topics. The authors are from many countries all over the world and this clearly shows that the soybean research and applications are of global significance.

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